

INSTABILITY OF SUPPORTED-PLATINUM SURFACE AREA
IN THE PRESENCE OF ELECTROLYTES

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Supported platinum crystallites grow rapidly when in contact with electrolyte solutions at moderate temperatures ($< 200^{\circ}\text{C}$). The absence of any growth in air at much higher temperatures indicates that the rate of area loss in solution is orders of magnitude greater than that of losses from dry sintering. This type of platinum-area loss is a serious handicap to the development of economic fuel-cell electrodes.

Measurements of platinum area, independent of the support area, were made by using a combination of integral capacitance measurements in the hydrogen-adsorption and double-layer regions. The possibility of poisoning was eliminated by checking the degree of crystallite growth with x-ray diffraction. Analyses showed that permanent dissolution of platinum was not a significant factor.

In addition to the effects of time and temperature, the rate of crystal growth was influenced by the support type, the solution, the platinum concentration, and the initial crystallite size. High support areas reduced crystal growth rates as did solutions with low conductivity. However, even water (10^{-4} mho/cm) showed some effect. The best dispersions are the most easily damaged because the very small initial crystallite size provides a large driving force for recrystallization. In such cases platinum-area losses up to 90% were observed.

Electrorecrystallization provides a possible mechanism for rationalizing these results; i.e., cells may be formed between large and small platinum crystallites, with the smaller crystallites acting as anodes because of their higher surface energies. Complex platinum ions would then be transported through the solution while electrons pass through platinum-platinum contacts, or through a conducting support, or through both. The transport of platinum complexes with no necessity for electron flow between crystallites would also be conceivable.